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PALLADIUM(II) AND PLATINUM(II) COMPLEXES OF UNSATURATED TERTIARY PHOSPHINES

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Summary

A series of square planar Pd^{II} and Pt^{II} complexes of the type $MX_2(L)$ [X = Cl, Br, I and L = $Ph_nP(CH_2CH_2CH{=}CH_2)_{3-n}$; n = 0-2] have been prepared and studied by ^1H and ^{31}P magnetic resonance, and infrared and Raman spectroscopy. The strength of the metal—olefin bond is found to be in the order Pt > Pd. When L = $PhP(CH_2CH_2CH{=}CH_2)_2$ or $P(CH_2CH_2CH{=}CH_2)_3$, IR and Raman data indicate only one olefin is coordinated in both the solid state and solution. On the PMR timescale, the olefins undergo rapid intramolecular exchange, offering a system in which one observes average H—H and Pt—H coupling.

Introduction

A marked difference in the reactivity of arylphosphine—olefin ligands and their alkenyl analogs in rhodium(I) and molybdenum(0) systems has been observed [1, 2]. Therefore we undertook the preparation of palladium(II) and platinum(II) complexes of the ligands 3-butenyldiphenylphosphine (mbp), di-3-butenylphenylphosphine (dbp), and tri-3-butenylphosphine (tbp) in order to compare metal—olefin interactions using spectroscopic methods. The identification of the strength of these interactions is essential to the understanding of homogeneous catalytic processes involving metal—olefin bonds.

Nyholm et al., using the ligands, o-$Me_2AsC_6H_4CH_2CH{=}CH_2$ [3], o-$Me_2AsC_6H_4CH{=}CH_2$ [4, 7], o-$Ph_2PC_6H_4CH{=}CH_2$ [3, 6], and o-$P(C_6H_4CH{=}CH_2)_3$ [8], have prepared complexes of the type $MX_2(L)$ (M = Pt and Pd, X = Cl and Br) whereas $Ph_2P(CH_2)_3CH{=}CH_2$ and $Me_2As(CH_2)_3CH{=}CH_2$ give a chelate complex only for platinum [5]. Infrared spectra have shown $\Delta\nu(C{=}C)$ on complexation for the palladium and platinum complexes to be ca. 100 and 140 cm^{-1} respectively. Proton magnetic resonance spectra have been reported only for $PtBr_2$-(o-$Me_2AsC_6H_4CH{=}CH_2$) and $PtBr_2[o$-$P(C_6H_4CH{=}CH_2)_3]$, and in the latter compound part of the olefin information is obscured by phenyl resonances. ^1H or

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^{31}P magnetic resonance information has not been reported for palladium complexes with this type of ligand. Haszeldine et al. [9] have recently reported the preparation of $PdCl_2(mbp)$ and $PtCl_2(mbp)$. However, they give no PMR data for the palladium complex and incorrect data for the platinum complex.

Experimental

Infrared spectra were recorded on a Perkin—Elmer 621 spectrometer using the He—Ne laser excitation at 6328 Å. Proton magnetic resonance spectra were obtained on a Varian HR 220 spectrometer. ^{31}P spectra were obtained at 40.5 MHz on a Varian XL-100 spectrometer. Molecular weights were determined in $CHCl_3$ on a Hewlett—Packard 302 vapor pressure osmometer. Analyses were carried out by Galbraith Laboratories, Knoxville, Tennessee. All reactions were carried out under an argon atmosphere, and all solvents were deaerated immediately prior to use. The compounds were found to be air and solution stable, but were found to decompose after several months in the solid state.

The starting materials, (norbornadiene)$PdCl_2$ [10], (cyclooctadiene)$PtCl_2$ [11], and the ligands mbp, dbp and tbp [12] were prepared by published methods.

Reaction of (norbornadiene)$PdCl_2$ with mbp, dbp and tbp

In a typical reaction, 5 mmol of ligand in 10 ml of $CHCl_3$ was added over a period of 1 h to 5 mmol of (norbornadiene)$PdCl_2$ in 25 ml of refluxing $CHCl_3$. The solution was heated at reflux for an additional 2 h and then cooled in an ice bath. The complex $PdCl_2(L)$ precipitated, was collected by filtration, washed with 10 ml of $CHCl_3$ and vacuum dried. The yield was typically 75-85% and the complexes can be recrystallized from benzene/hexane.

With a ligand-to-metal ratio of 2/1, the complexes $PdCl_2(L)_2$ were obtained in an analogous fashion with yields of 90-100%.

Preparation of $PdX_2(L)$ and $PdX_2(L)_2$ $L = mbp, dbp, tbp; X = Br, I$

In a typical reaction, 0.25 mmol of $PdCl_2(L)$ or $PdCl_2(L)_2$ was stirred for 2 h at room temperature with 2.5 mmol of LiBr or NaI in 25 ml of deaerated acetone. The solvent was subsequently removed under vacuum and the resulting solid extracted with two-25 ml portions of $CHCl_3$. The $CHCl_3$ was removed under vacuum and the complex recrystallized from benzene/hexane.

Reaction of (cyclooctadiene)PtX_2 ($X = Cl, Br$) with mbp

In a typical reaction, 5 mmol of mbp in 25 ml of $CHCl_3$ was added over a period of 2 h to a suspension of 5 mmol of (cyclooctadiene)PtX_2 in 25 ml of refluxing $CHCl_3$. The solution was heated at reflux for an additional five hours and then concentrated to ca. 10 ml. Upon addition of 10 ml of isooctane, a glassy solid formed which was recrystallized from dichloromethane/isooctane to obtain a white powder, which contained 5-10% $PtX_2(mbp)_2$ and 80-90% $PtX_2(mbp)$, as observed from PMR integration. Further purification could not be achieved.

Reaction of (cyclooctadiene)PtI_2 with mbp, dbp and tbp

In a typical reaction, 5 mmol of (cyclooctadiene)PtI_2 was suspended in

20 ml of refluxing $CHCl_3$ and 5 mmol of ligand was added over a period of 2 h. The solution was heated at reflux for an additional 6 h and then concentrated to ca. 5 ml. The addition of 5 ml of isooctane produced a yellow microcrystalline material which was collected by filtration, recrystallized from $CHCl_3$/isooctane and dried. The yield of $PtI_2(L)$ typically was 75%.

When a ligand-to-metal ratio of 2/1 was used the complexes $PtI_2(L)_2$ were obtained in 90-100% yield using the same procedure.

Discussion

Reaction of mbp with (norbornadiene)$PdCl_2$ resulted in the formation of the complex $PdCl_2$(mbp). The insolubility of this complex required use of a computer of average transients (CAT) on an HR 220 spectrometer. The spectrum shown in Fig. 1 was obtained after 250 scans. CAT scanning on the remaining palladium complexes was not necessary due to increased solubility when the halide or ligand was changed. When iodide metathesis was attempted, only dimeric palladium complexes containing non-bonded olefin were obtained. Nyholm [3] found similar dimerization occurred in an attempt to prepare $PdI_2(o\text{-}Me_2AsC_6H_4CH{=}CH_2)$.

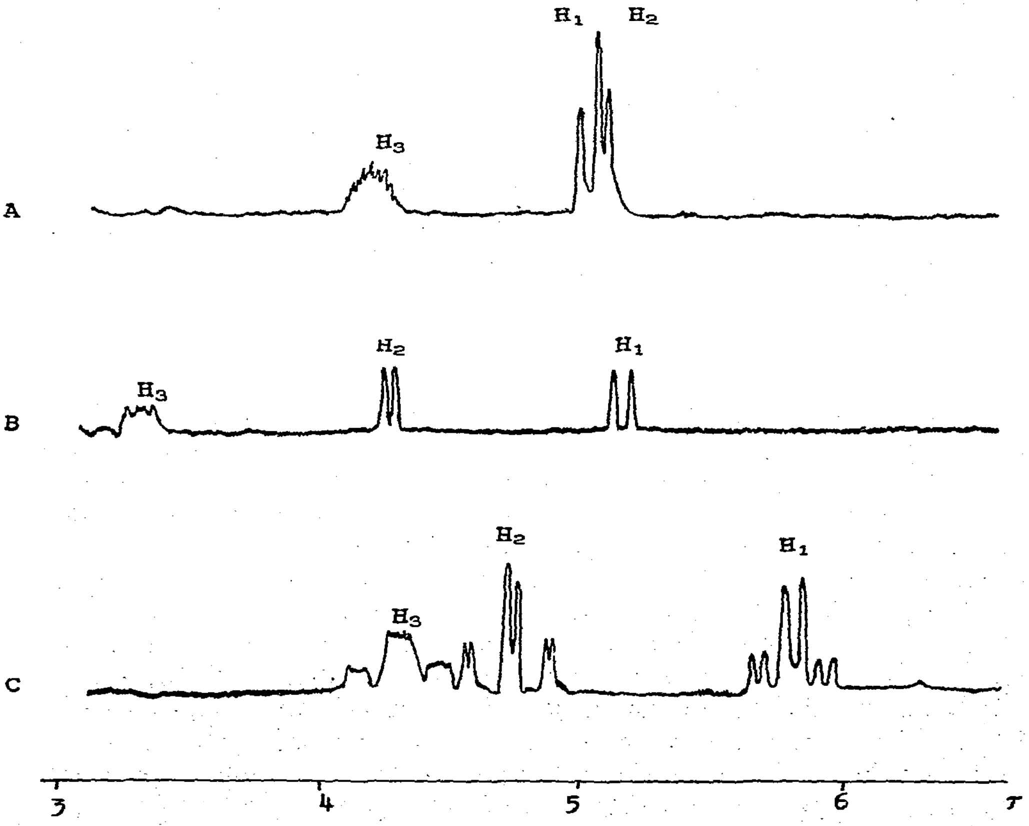


Fig. 1. 220 MHz PMR spectra of: (A) mbp, (B) $PdCl_2$(mbp), (C) PtI_2(mbp).

TABLE 1

ANALYTICAL DATA OF Pd^{II} AND Pt^{II} PHOSPHINE—OLEFIN COMPLEXES

Complex	Found (calcd.) (%)		Mol. wt. found (calcd.)
	C	H	
$PdCl_2$(mbp)	45.74 (46.04)	4.20 (4.08)	430 (417)
$PdBr_2$(mbp)	37.92 (37.95)	3.35 (3.36)	482 (506)
[PdI_2(mbp)]$_2$	31.75 (32.00)	2.87 (2.83)	1125 (1200)
$PdCl_2$(dbp)			410 (395)
$PdBr_2$(dbp)	34.64 (34.71)	3.93 (3.93)	487 (484)
$PdCl_2$(tbp)	38.34 (38.70)	5.57 (5.65)	386 (372)
$PdBr_2$(tbp)			450 (462)
$PdCl_2$(mbp)$_2$	57.83 (58.54)	5.15 (5.18)	683 (656)
$PdCl_2$(dbp)$_2$	54.17 (54.90)	6.14 (6.21)	583 (612)
$PdCl_2$(tbp)$_2$	49.93 (50.70)	7.23 (7.39)	552 (568)
PtI_2(mbp)	27.43 (27.79)	2.64 (2.46)	672 (691)
PtI_2(dbp)	25.32 (25.19)	2.83 (2.84)	658 (667)
PtI_2(tbp)	21.92 (22.33)	3.17 (3.41)	639 (645)
PtI_2(mbp)$_2$	40.75 (41.16)	3.52 (3.64)	887 (933)

The platinum complexes were not easily prepared. Reactions were attempted with (cyclooctadiene)PtX_2, (norbornadiene)PtX_2 and PtX_2 (X = Cl and Br), giving mixtures of PtX_2(mbp) and PtX_2(mbp)$_2$. Other unidentified materials were obtained when $PtCl_2$ was used. Careful, slow addition of mbp to (cyclooctadiene)PtX_2 (X = Cl and Br) resulted in the desired complexes contaminated by small amounts of (cyclooctadiene)PtX_2 and PtX_2(mbp)$_2$. Analyses of PtX_2(mbp) (X = Cl and Br) were not satisfactory, but their PMR signals could be assigned by comparison with the spectra of PtI_2(mbp) and the aforementioned contaminants. The iodides, on the other hand, were easily prepared by slow addition of the ligands to (cyclooctadiene)PtI_2.

Infrared data

In recent years there has been controversy over the assignment of bonded olefin stretching frequencies [13—16]. Recently, Powell has shown that the absorption at ca. 1500 cm^{-1} (band I) is primarily due to the ν(C=C) stretch and that the C—H deformation is mainly responsible for the absorption at ca. 1250 cm^{-1} (band II). The absorptions are coupled and are found to be weak in the infrared and of medium intensity in the Raman. For a series of isostructural cyclooctadiene complexes, Powell [18] concluded that a stronger metal—olefin bond is reflected in lower olefinic stretching frequencies.

Infrared and Raman data for the palladium(II) and platinum(II) phosphine—olefin complexes are tabulated in Table 2. When uncomplexed, the olefins exhibit a medium intensity absorption in both the infrared and Raman spectra at ca. 1639 cm^{-1}. When complexed, band I occurs as a weak absorption in the infrared and a medium absorption in the Raman [ca. 1525 for palladium(II) and 1495 cm^{-1} for platinum(II)]. Band II occurs in the infrared as a partially obscured weak absorption for both the palladium(II) and platinum(II) complexes.

TABLE 2

INFRARED AND RAMAN DATA (cm^{-1})

Compound	Infrared[a]			Raman[b]		
	Free olefin	Band I	ν(Pd—Cl)	Free olefin	Band I	Band II
$PdCl_2(mbp)$		1525 w	323s, 291s		1525m	1239m
$PdBr_2(mbp)$		1525w				
$PdCl_2(dbp)$	1639m	1525w	309s, 277s	1639m	1525m	1244m
$PdBr_2(dbp)$	1639m (1636)	1526w (1528)				
$PdCl_2(tbp)$	1639m	1528w	333s, 263s	1639m	1526m	1247m
$PdBr_2(tbp)$	1639m (1635)	1528w (1529)				
$PdCl_2(mbp)_2$	1638m		350s	1639m		
$PdCl_2(dbp)_2$	1638m (1635)					
$[PdI_2(mbp)]_2$	1638m					
$PtI_2(mbp)$		1495w				
$PtI_2(dbp)$	1639m (1636)	1496w (1493)				
$PtI_2(tbp)$	1639m (1636)	1495w (1495)				
$PtI_2(mbp)_2$	1639m					

[a] Pd complexes in nujol; Pt complexes in fluorolube; solutions in ($CHBr_3$). [b] As powdered solids.

Band II can be observed in the Raman spectra at ca. 1245 cm^{-1} for the palladium(II) complexes. Unfortunately the platinum(II) complexes decomposed in the laser beam in both the solid state and in solution, precluding proper identification of band II. The assignment of the metal—carbon symmetric and asymmetric stretching frequencies also has been used in the study of olefin complexes [18]. However, analyses of the spectra in the region 600-200 cm^{-1} did not allow an unambiguous assignment of these absorptions.

The complexes $MX_2(L)$ were assigned a *cis* structure in the solid state in consideration of the steric restriction imposed by chelation and the two strong M—Cl stretches found for the palladium(II) complexes. The complex $PdCl_2(mbp)_2$ has one M—Cl stretch and was thus assigned a *trans* configuration (see ^{31}P discussion later).

PMR data

The limited PMR data available for platinum(II) and palladium(II) olefin complexes indicate the olefinic protons are at best only slightly shielded versus free ligand values [20]. Data of palladium olefin complexes are particularly scant. Clarke et al. [21] have observed deshielding of the vinylic protons for complexes of norbornadiene and bicyclo[3.3.1]none-2,5-diene. Recently Ugo et al. [22] have observed deshielding in a palladium(II) complex of 1-pentene.

Olefin complexation for most transition metals results in net shielding of the olefinic protons [23]. The olefin complexes of silver(I), which exhibit net deshielding of their protons, are an exception to this rule. This is presumably due to a predominance of the σ component over the π component in the metal—

olefin bond [24]. The olefin protons of the phosphine—olefin ligands of platinum(II) are slightly shielded (Table 3), but for palladium(II) the H_2 and H_3 protosn are deshielded. Thus, deshielding appears to be common for both palladium(II) and silver(I), even though the *overall* metal—olefin bond strength is considerably larger for palladium(II). The stronger bond is best reflected by the reduction of the *cis* and *trans* coupling constants upon complexation of the olefin. For silver(I) the sum of the reductions is only 1.0 Hz [24], for palladium(II) it is 4.1 Hz and for platinum (II) it is 5.5 Hz. These changes also parallel the changes in ν(C=C) and support the conclusion that the metal—olefin bond strengths are in the order silver(I) < palladium(II) < platinum(II).

The relationship between chemical shifts and coupling constants for a bonded olefin can also be observed by changing the halide of the complex. In going from chloride to bromide in PdX_2(mbp) the downfield shifts accompany the larger J_{13} and J_{23}. For the platinum complexes the lowest chemical shift and the largest coupling constants are observed when X = I. Thus the strongest metal—olefin bond is formed when chlorine is the halide *trans* to the olefin. This trend has previously been reported for complexes of the type *cis*-$PtX_2(R_3P)(C_2H_4)$ [25].

Although the ligands dbp and tbp can serve as tri- and tetradentate ligands respectively, upon coordination of platinum(II) and palladium(II), they act only as bidentate chelates. Solution IR spectroscopy shows that only one olefin is coordinated in both the palladium and platinum complexes. On the slower time scale of the PMR observations, only one set of resonances is observed, indicating rapid exchange of the olefins in solution. The most likely mechanism is intramolecular exchange through a five-coordinate intermediate.

An average olefin environment on the PMR time scale is manifested in the chemical shifts and coupling constants. The average environment for the chemical shifts is observed easily in the H_3 resonances of the palladium chloride series. For $PdCl_2$(mbp), where the ligand is chelated, the resonance is at 3.33 τ. In $PdCl_2(mbp)_2$, where there are two non-chelating ligands, the resonance is at 4.20 τ. For $PdCl_2$(dbp) the resonance at 3.83 τ is midway between the bonded and non-bonded values, which is consistent with coordination of each olefin one-half of the time. The resonance at 4.00 τ for $PdCl_2$(tbp) indicates coordination of each olefin only one-third of the time. The same trend is observed in the series PtI_2(mbp), PtI_2(dbp) and $PtI_2(mbp)_2$ where the H_3 resonance at 4.32 τ for PtI_2(dbp) is exactly midway between free and bonded values.

The rapid olefin exchange is also apparent in the coupling constants of the series PtI_2(mbp), PtI_2(dbp), PtI_2(tbp) and $PtI_2(mbp)_2$. A J_{23} of 9.1 Hz for PtI_2(dbp) is midway between the free value of 10.0 Hz and bonded value of 8.2 Hz. The PtI_2(tbp) value of 9.5 Hz indicates coordination of each olefin one-third of the time.

The olefin exchange is also reflected in J(Pt—H_1) and J(Pt—H_2). The couplings are too small to be resolved for the free ligand, but are 60 and 71 Hz respectively for PtI_2(mbp) and 29.36 and 20.24 Hz for the dbp and tbp complexes. The latter two values again indicate coordination of the olefin one-half and one-third of the time. Nyholm observed an average Pt—H coupling for $PtBr_2[o\text{-}P\text{-}(C_6H_4CH{=}CH_2)_3]$ [8], but was unable to interpret it at the time. J(Pt—H_3) is 67 Hz for PtI_2(mbp) and 34 Hz for PtI_2(dpb). The coupling constant in PtI_3(tbp) could not be discerned due to the line width of the H_3 resonance. In all cases, platinum satellites are observed in the ratio 1/4/1 due to a small (< 1 Hz) coupling being transmitted to the olefinic protons through the ligand backbone.

Since five- and even six-coordination in platinum(II) and palladium(II) has been observed [26], the possibility that olefins in complexes such as $MCl_2(L)$ (L = dbp or tbp) are forming one strong and one or two weak bonds should be considered. The complexes $MCl_2(L)_2$ also could be using a fifth or sixth coordination site to form very weak bonds to the olefin. Examination of the IR spectrum of $PdCl_2(dbp)_2$ reveals only one olefin absorption at the free ligand value both in solution and in the solid state. Examination of the H_1 and H_2 resonance of the complex $PtI_2(mbp)_2$ reveals, by linewidth measurements, that any Pt—H coupling must be less than 4 Hz. Thus, although very weak olefin bonding cannot be thoroughly discounted, its presence has not been observed in any of the compounds by these physical measurements.

The methylene protons H_4 and H_5 yield a complex pattern in the 7—9 τ region. Non-equivalence is best observed for the H_4 and/or H_5 protons in the complexes $PdCl_2(mbp)$, $PtI_2(dbp)$ and $PdCl_2(tbp)_2$, due to larger chemical shift differences. Coupling constant information was not obtained at this time.

Phosphorus coupling to H_1 and H_2, which has recently been observed by Bennett [27] as 2.5 Hz in the complex $Mo(CO)_4$(*o*-$Ph_2PC_6H_4CH{=}CH_2$) is less than 1 Hz in the palladium(II) and platinum(II) complexes. In our study of Mo^0 complexes [2] this coupling was also less than 1 Hz.

An attempt was made to stop the olefin exchange process on the complexes $PdCl_2(tbp)$ and $PtI_2(tbp)$. At —50° some broadening was observed in the PMR, but the exchange process was not stopped.

Phosphorus-NMR data

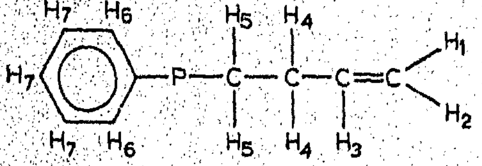
^{31}P data are tabulated in Table 3. Phosphorus chemical shifts in metal—tertiary phosphine complexes are not well understood theoretically [28—30]. A comparison of our complexes $MX_2(L)$ (see Table 3) with complexes of the type *cis*-$MCl_2(L)_2$ [$M = Pt, Pd; L = Ph_xP(CH_2CH_2CH_2CH_3)_{3-x}; x = 0\text{-}3$] reveals rather large ca. 50 ppm downfield shifts for the palladium complexes and ca. 35 ppm downfield shifts for the platinum complexes. More is known about the reasons for the magnitude of the Pt—P coupling constant. Pidcock [29] has observed, for a given phosphorus ligand, that the coupling constant in different complexes is mainly determined by the nature of the ligand *trans* to the phosphorus and less affected by the ligands in the *cis* position. For square planar platinum(II) complexes, larger coupling constants have been related to stronger platinum—phosphorus bonds [33].

In comparing *cis*-$PtI_2[P(C_4H_9)_3]_2$ [33] with $PtI_2(tbp)$ the *J*(Pt—P) decreases from 3372 to 2934 Hz. The major differences between these two complexes are a *cis* substitution of an olefin for a trialkylphosphine and the prevention of rotation about the platinum—phosphorus bond due to chelation. This large reduction in *J*(Pt—P), and presumably the platinum—phosphorus bond strength, was unexpected for the *cis* substitution.

Examination of the ^{31}P spectra of $PdCl_2(mbp)_2$ shows resonances at —15.8 (*trans*) and —26.6 ppm (*cis*) differing less than 0.5 ppm from the *cis* and *trans* values given by Grim [32] for $PdCl_2(Ph_2PCH_2CH_2CH_2CH_3)_2$. The intensities of the two resonances were in *trans*/*cis* ratio of ca. 10/1.

TABLE 3

220 MHz NMR SPECTRA OF Pd^{II} AND Pt^{II} PHOSPHINE–OLEFIN COMPLEXES[a]



Compound	τ_1	τ_2	τ_3	τ_4	τ_5	τ_6	τ_7	J_{13}	J_{23}	J(Pt–H$_1$)	J(Pt–H$_2$)	J(Pt–H$_3$)	δ_P[d]	J(Pt–P)
mbp	5.06	5.11	4.19	7.9[b]		2.60	2.70	17.0	10.0				16.5	
dbp	5.00	5.08	4.17	7.92	8.20	2.52	2.68	17.0	17.0				25.4	
tbp	4.97	5.04	4.15	7.83	8.51			17.10	10.20				30.2	
$PdCl_2$(mbp)	5.17	4.26	3.33	7.62 7.51	7.28	2.17	2.44	14.6	8.3					
$PdBr_2$(mbp)	4.91	4.04	3.22	7.48[b]		2.17	2.50	14.8	8.5				−57.1	
[PdI_2(mbp)]$_2$	4.95[b]		4.20	7.62	7.15	2.34	2.55							
$PdCl_2$(dbp)	5.12	4.75	3.83	7.52[b]		2.06	2.52	15.6					−65.4	
$PdBr_2$(dbp)	5.06	4.60	3.75	7.53[b]		2.05	2.38	15.7						
[PdI_2(dbp)]$_2$	4.95[b]		4.19	7.44	7.70	2.38	2.56							
$PdCl_2$(tbp)	5.00	4.77	4.00	7.54	7.78			16.2	9.4				−76.3	
$PdBr_2$(tbp)	4.95	4.66	3.93	7.52	7.73			16.2	9.4					
[PdI_2(tbp)]$_2$	4.84[b]		4.16	7.46[b]										
$PdCl_2$(mbp)$_2$	5.04[b]		4.20	7.76	7.48	2.27	2.54						−15.8, −26.6	
$PdCl_2$(dbp)$_2$	4.96[b]		4.18	7.65[b]		2.31	2.56							
$PdCl_2$(tbp)$_2$	4.93[b]		4.18	7.68	8.00 7.89									
$PtCl_2$(mbp)	6.10	5.29	4.61	7.60[b]		2.06	2.55	13.5	8.0					
$PtBr_2$(mbp)	6.04	5.06	4.50	7.63[b]		2.04	2.53	13.5	8.0					
PtI_2(mbp)	5.82	4.75	4.42	7.65[b]		2.03	2.52	13.7	8.2	60	71	67	−34.1	3071
PtI_2(dbp)	5.40	4.88	4.32	7.59	7.96 7.59	2.15	2.55	15.0	9.1	29	36	34	−37.8	3032
PtI_2(tbp)	5.25	4.91	4.34	7.78[b]				16.0	9.5	20	24	[c]	−42.1	2934
PtI_2(mbp)$_2$	5.10	4.96	4.22	7.70	7.02	2.35	2.65	17.0	10.0					

[a] All spectra taken in $CDCl_3$; all values for dbp and tbp complexes are average values due to exchange. [b] Center of unresolved multiplet. [c] Obscured by 28 Hz line width of H_3. [d] In ppm vs. 85% H_3PO_4.

Conclusions

The alkenyl phosphine derivatives of palladium(II) and platinum(II) are in all cases analogous to the aryl derivatives. This result is unlike that previously reported for molybdenum(0) where the reaction chemistry differed significantly between the alkenyl and aryl complexes [2]. It has been shown [2] previously that $\Delta\nu$(C=C) for $Mo(CO)_4$(mbp) and $Mo(CO)_4(o\text{-}Ph_2PC_6H_4CH{=}CH_2)$ are 102 and 120 cm^{-1}, possible indicating a weaker olefin interaction in the former compound. For palladium(II) and platinum(II), the $\Delta\nu$(C=C) for the alkenyl and aryl complexes are the same ca. 110 and 140 cm^{-1}. These results can be interpreted as indicating that the orbitals of molybdenum have differing degrees of overlap with the σ- and π^*-orbitals of the olefins present in the alkenyl and aryl ligands, which result in bonds of different strength. For palladium(II) and platinum(II) however, the use of these orbitals must be more nearly equal since the alkenyl and aryl bond strengths, as inferred from $\Delta\nu$(C=C), are approximately the same.

IR, PMR and Raman measurements indicate mbp, dbp and tbp act as bidentate ligands in square planar palladium(II) and platinum(II) complexes rather than form complexes which are five- or six-coordinate. On the PMR timescale, rapid intramolecular olefin exchange which causes averaging in the chemical shifts, Pt—H and H—H coupling is observed. PMR spectra of the Pd olefin complexes show net deshielding of the olefinic protons. From comparison of coupling constants, chemical shifts and band I in the IR and Raman spectra, we conclude that the metal—olefin bond strength is in the order platinum > palladium.

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